# Adsorbate Azimuthal Orientation from Reflectance Anisotropy Spectroscopy

B. G. Frederick,* J. R. Power, R. J. Cole, C. C. Perry, Q. Chen, S. Haq, Th. Bertrams,
N. V. Richardson,† and P. Weightman

*IRC in Surface Science, University of Liverpool, Liverpool L69 3BX, United Kingdom*
(Received 9 December 1997)

We have determined the azimuthal orientation of an adsorbate on a metal surface from an intramolecular-transition-derived feature in reflectance anisotropy spectroscopy (RAS). Adsorption of 9-anthracene carboxylic acid onto $p(2 \times 1)$O/Cu(110) led to an ordered structure with a strong (2%), derivativelike feature at 4.5 eV. Fresnel theory predicts the measured intensity, functional behavior, and sense of the RAS signal for the molecule aligned along [110]. IR measurements confirm that the molecular plane is perpendicular to the surface and STM measurements support the azimuthal orientation. We reassign the sense of the clean Cu(110) surface RA spectrum. [S0031-9007(98)06135-3]

Reflectance anisotropy spectroscopy (RAS), also known as reflectance difference spectroscopy (RDS) using linearly polarized, visible light to detect azimuthal dependence in surface structure, has evolved from fundamental semiconductor surface studies to the control of semiconductor processing *in situ* under higher pressures and with real-time feedback [1]. Early applications of the technique to metal surfaces showed strong anisotropy of fcc (110) surfaces associated with transitions between surface states as well as interband transitions in the near surface region [2,3]. Recently, there have been several attempts to follow the effects of molecular adsorption on metal surfaces [4–7]. Although the molecule-surface bond clearly modifies the inherent anisotropy of the substrate metal electronic states, the information is not directly interpretable and may contain little information regarding the orientation of nonbonding moities in multifunctional species. To date, none of the adsorbates studied [4–6,8] have shown an intramolecular electronic transition within the 1.5–5.5 eV energy range available. To demonstrate the potential of RAS, we chose a larger conjugated molecular species, so as to shift the intramolecular electronic transitions into the visible region. We report here the first observation of reflectance anisotropy originating from an intramolecular transition, following the adsorption of 9-anthracene carboxylic acid (9-AA) onto the $p(2 \times 1)$O/Cu(110) surface, with a structure approximately described as $p(8 \times 1)g$. No previous studies of this adsorption system exist.

In principle, the azimuthal orientation of an adsorbate can be determined from the RA spectrum if a well-defined transition dipole, relative to the molecular coordinates, exists within the available energy range and the metal does not screen the E field of the light parallel to the metal surface. In favorable cases, such as the one chosen here, the application of RAS to molecular adsorbates requires understanding (i) the *intensity;* (ii) whether an adsorbate transition causes an *increase* or *decrease* in reflectivity, since the sense corresponds to a rotation of the adsorbate by 90°, and (iii) whether or not Fresnel equations, which

are valid in the continuum limit, apply at microscopic dimensions and describe the substrate response adequately.

9-Anthracene carboxylic acid (Aldrich; %99) is a low volatility, yellow, organic solid, and was introduced to the UHV system via a line-of-sight dosing system similar to that described previously [9]. The sublimation temperature of the solid, 335–345 K, was monitored with an *in situ* chromel-alumel thermocouple. The Cu(110) crystal was mechanically and electrochemically polished and then cleaned by cycles of Ar ion (500 eV) bombardment and annealing (700 K) until a sharp $(1 \times 1)$ LEED pattern was obtained. The RA spectrometer [10], which utilized normal incident, linearly polarized light at 45° to the high symmetry direction and analyzed the reflected light with a photoelastic modulator (Hinds), Rochan polarizer, monochromator and lock-in detection, was coupled to a UHV system, through a strain-free window. Experimental artifacts were removed from the raw data using a correction function determined by measuring RA spectra with the [110] direction aligned in two orthogonal orientations at 45° to the polarization direction. The RA ($\Delta r/r$) is defined as

$$\frac{\Delta r}{r} \left( \equiv \mathrm{Re}(\omega) - i \,\mathrm{Im}(\omega) \right) = 2 \frac{r_{[110]} - r_{[001]}}{r_{[110]} + r_{[001]}}, \quad (1)$$

where $r_x$ is the complex Fresnel amplitude for reflection of light polarized in the $x$ direction. The real RA spectrum of the Cu(110) surface before and after saturation with oxygen at room temperature to form the $p(2 \times 1)$O structure is shown in Fig. 1. The sharp feature at 2.1 eV, has been assigned previously [5,6] to a transition at $\bar{Y}$ between a filled surface state approximately 0.15 eV below the Fermi level and an unoccupied surface state about 1.85 eV above the Fermi level. That this is indeed a surface state transition is clear from its decay with adsorption, as shown in the inset. The anisotropy at 2.1 eV decreases during dosing, but recovers slightly near saturation coverage as seen previously for a number of adsorbates on Cu(110) [5,6]. The spectrum of the $p(2 \times 1)$O/Cu(110) surface, Fig. 1(b), is

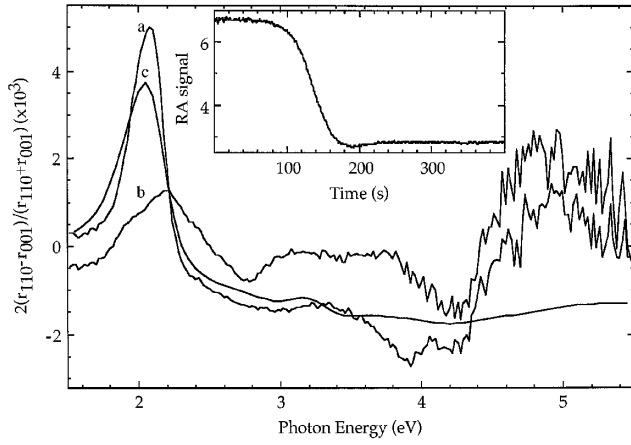FIG. 1. Real RA spectra, Re($\omega$), of curve (*a*) the clean Cu(110) surface and curve (*b*) after saturation exposure to oxygen resulting in the $p(2 \times 1)$O reconstruction. Curve (*c*): Model calculation of the clean Cu(110) RA spectrum in which a single Lorentzian oscillator was placed in $\epsilon^{[001]}$ at 2.1 eV with FWHM = 0.5 eV, $\epsilon^{[110]} = 1$, and measured optical constants [17] were used for the copper substrate in a three layer Fresnel calculation [11,12]. The inset shows measured temporal behavior at 2.1 eV during oxygen exposure.

in good agreement with previous work [6]. However, for the sense of the anisotropy defined in Eq. (1), we plot the clean Cu(110) RA spectrum with the 2.1 eV feature in the *upward* direction, opposite that suggested by Hofmann *et al.* [6], in view of two considerations. First, although there is general agreement that the dipole transition is allowed only for light polarized along [001], the response of the substrate determines whether the reflectivity *increases* or *decreases*. As discussed in greater detail elsewhere for a range of materials [11], Re($\omega$) and Im($\omega$) for a three-phase thin film system [12] contain contributions from both the real and imaginary parts of the complex surface dielectric anisotropy $\Delta \tilde{\epsilon}_a = \tilde{\epsilon}_a^{[110]} - \tilde{\epsilon}_a^{[001]}$:

$$\text{Re}(\omega) = -\frac{2\omega d}{c} \left\{ A(\omega)\Delta \epsilon_a''(\omega) + B(\omega)\Delta \epsilon_a'(\omega) \right\}, \quad (2)$$

$$\text{Im}(\omega) = \frac{2\omega d}{c} \left\{ A(\omega)\Delta \epsilon_a'(\omega) - B(\omega)\Delta \epsilon_a''(\omega) \right\}, \quad (3)$$

where $d$ is the film thickness, $c$ the speed of light, and $A(\omega)$ and $B(\omega)$ are real functions determined solely by the substrate dielectic function, $\tilde{\epsilon}_s = \epsilon_s' - i\epsilon_s''$:

$$A(\omega) - iB(\omega) = \frac{1}{1 - \tilde{\epsilon}_s(\omega)} = \frac{[1 - \epsilon_s'(\omega)] - i\epsilon_s''(\omega)}{|1 - \tilde{\epsilon}_s(\omega)|^2}. \quad (4)$$

Below the $d$-band edge, copper behaves like a free-electron metal ($|A| > B, A > 0$ [11]), in which an absorption in a surface layer leads to a *decrease* in reflectivity and therefore a positive-going feature for an absorption polarized along [001], as shown in Fig. 1(c). Furthermore, the presence of an anisotropic surface layer amplifies features in

the substrate optical response leading to behavior in the 4 eV region remarkably reminiscent of the measured spectrum, despite the simplicity of the model, and demonstrates [11] the ability of the substrate to influence RA spectra. Second, the sense of the anisotropy is also in agreement with calculations of Ag(110) and Au(110) RA derived from bulk $d$ to $s$-$p$ interband transitions [2,3], if the feature at 2 eV is associated with absorption at the $d$-band edge. Although the transition at $\bar{Y}$ provides *one* mechanism for the surface differential anisotropy, it is still not clear if this is the *dominant* mechanism [13]. The 9-AA results presented here, however, are consistent with this revised definition of the clean surface anisotropy.

A set of RA spectra acquired while dosing the saturated $p(2 \times 1)$O/Cu(110) surface at 300 K with 9-AA is shown in Fig. 2(A). Initially (curves *b,c*), a feature grew near 4.5 eV, but with increasing coverage (curves *e–g*), became a strong, negative going feature. Upon annealing, the anisotropy continued to grow, as shown in Fig. 2(B). After annealing to the indicated temperatures, the sample was cooled but showed no change in the RA spectrum, indicating irreversible improvements in the azimuthal ordering of the surface. Heating beyond 430 K resulted in thermal decomposition of the adsorbate and loss of the strong features in the RA spectrum.

A single reflection IR spectrum, shown in Fig. 2(C), after dosing of 9-AA onto $p(2 \times 1)$O/Cu(110) and annealing to 350 K showed only vibrational modes of $A_1$ symmetry under the $C_{2v}$ point group. These bands derive from the $B_{1u}$ modes of anthracene ($D_{2h}$) and the totally symmetric modes of the carboxylate group, demonstrating that an upright carboxylate species occurs at all coverages, as found for benzoate [14] and 3-thiophene carboxylate [7] on the $p(2 \times 1)$O/Cu(110) surface. In principle, given the upright orientation determined from IR and the substrate optical response, the azimuthal orientation of the molecules can be determined. However, due to the nature of the difference measurement in RAS, an estimate of the intensity when all molecules are perfectly aligned is required to determine the (average) azimuthal orientation.

A simple estimate of the *magnitude* which may be expected in RAS can be obtained from the following considerations. Figure 3 shows a UV-visible spectrum of 9-AA in methanol, which is essentially the same as that for anthracene [15]. The most intense band (254 nm = 4.8 eV) is the $^1B_{2u}$-$^1A_{1g}$ $\pi$ to $\pi^*$ transition [16], which is active when the light is polarized along $y$, the long axis of the aromatic system. The sequence of bands of lesser intensity between 3.2 and 4 eV derive from the $^1B_{1u}$-$^1A_{1g}$ transition by vibronic coupling and are polarized along $z$. For the upright species, only the $y$ polarized transition at 4.8 eV can be excited at normal incidence. The maximum strength of the intramolecular-transition-derived RAS feature at 4.5 eV can be estimated from the absorptivity of the parent molecule, where the absorbance, $A = \epsilon Cl$, where $C$ is the concentration, $l$ is the path length, and the
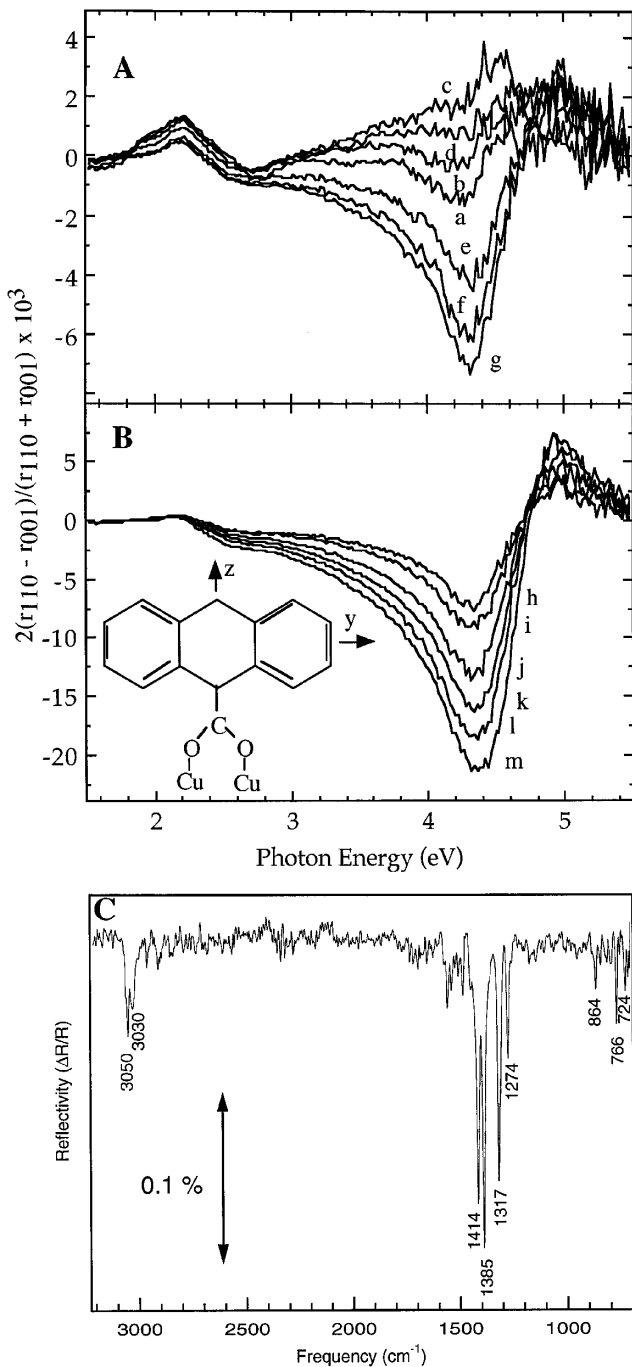
FIG. 3.   Comparison of the UV-visible absorption spectrum of 9-AA in methanol with calculations of $Re(\omega)$ (solid curve) and $Im(\omega)$ (dashed) for a layer of anthracene on an isotropic copper substrate [17] with $\epsilon_L \parallel [110]$ and $\epsilon_N \parallel [001]$.

light is absorbed by the oriented molecules in only one polarization, then $\Delta r/r = 0.109$ [Eq. (1)].

A more realistic estimate of the effect of the substrate on the RA response can be obtained from Fresnel equations using measured optical constants for copper [17]. Although copper behaves like a free electron metal below the $d$-band edge, its optical response above the edge ($B > |A|; A > 0$ [11]) causes $Re(\omega)$ to resemble $-\Delta\epsilon_a'$ [see Eq. (2)], while $Im(\omega)$ resembles $-\Delta\epsilon_a''$ [Eq. (3)]. Figure 3 shows a calculation of $Re(\omega)$ and $Im(\omega)$, using the measured dielectric functions of single crystal anthracene [16] with $\Delta\tilde{\epsilon}_a = \tilde{\epsilon}_L(\omega) - \tilde{\epsilon}_N(\omega)$. Here, $\tilde{\epsilon}_L(\omega)$ pertains to the long axis of the molecule $y$, and $\tilde{\epsilon}_N(\omega)$ is perpendicular to the molecule. The derivative shape in $Re(\omega)$ nicely reproduces the experimental spectra [Fig. 2(B)], implying that the long axis is preferentially aligned along [110]. We note that the intensity of the peak in $Im(\omega)$, 0.108, corresponds surprisingly well to our estimate above from the UV-visible absorptivity. However, the calculated intensity in the real part at 4.3 eV, $-0.08$, is about four times the maximum intensity observed, suggesting either azimuthal rotation of the anthracene ring away from the high symmetry direction or disordered, isotropic regions.

The LEED pattern, shown in Fig. 4(A) contains 1/8 order spots at $(n/8, \pm(1 - \delta))$, but only 4× periodicity within the [110] mirror plane, suggesting a glide line structure. To confirm the orientation suggested by the periodicity and the Fresnel theory, we have imaged the structure with STM. The structure contains rows of features, separated by one lattice constant along [001] and with 4× periodicity along [110] [Figs. 4(B), 4(C)]. The size of the anthracene molecule would indicate that, to achieve a 4× periodicity, the ring must rotate away from the [110] plane. However, the image in Fig. 4(B) suggests that adjacent rows appear to rotate in opposite directions, suggesting a $p(8 \times 1)g$ structure with the glide line along [110] as shown in the model of Fig. 4(D),



FIG. 2.   (A) Real RA spectra, $Re(\omega)$, while dosing 9-AA on $p(2 \times 1)O/Cu(110)$ to produce the carboxylate species shown in the inset.   Dosing times: (a) 0 min, (b) 4 min, (c) 8 min, (d) 12 min, (e) 16 min, (f) 27 min, (g) 51 min; (B) Spectra acquired after annealing to (h) 295 K, (i) 348 K, (j) 365 K, (k) 373 K, (l) 405 K, and (m) 430 K. (C) Infrared reflection absorption spectrum of the $p(8 \times 1)g$ structure at 350 K.

absorptivity,   $\epsilon(254 \text{ nm}) = 104\,800 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} = 1.74 \times 10^{-16} \text{ cm}^2/\text{molecule}$.   For the ideal $p(8 \times 1)g$ structure   with   $2.7 \times 10^{14} \text{ molecule/cm}^2$   [$\theta = 0.25$ monolayer (ML), see below], we expect the oriented molecules to have a maximum absorbance of 0.047, or $I/I_0 = 0.897$.   If the substrate is an ideal mirror and the
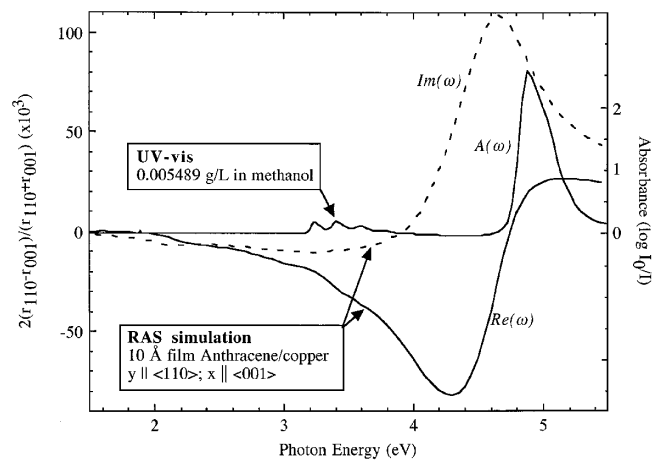
to absorb in the visible, on metal substrates for applications in which obtaining a high degree of orientation, such as in molecular electronics and organic film growth for nonlinear optical purposes, is critical.



FIG. 4. (*A*) LEED pattern and STM images: (*B*) 60 Å × 60 Å, $-0.35$ V, $0.47$ nA and (*C*) 350 Å × 510 Å of 9-AA/O/Cu(110) adsorbed at 350 K. (*C*) Model of an ideal $p(8 \times 1)g$ structure (unit cell shown) with the anthracene rings rotated by 15° from [110] to avoid steric repulsion.

constructed using van der Waals' radii about the centers of the projected atomic positions from the x-ray crystal structure of anthracene [18]. Rotation of the rings by about 15° from [110] alleviates the steric repulsion. Although the rotation will decrease the RA signal, disordered regions and defects probably account for a greater decrease in the RA signal, as STM showed that the extent of ordering was sensitively dependent on adsorption temperature.

In summary, we have detected anisotropy in the reflectivity in a 0.25 ML approximately $p(8 \times 1)g$ structure of 9-anthracene carboxylate formed on the $p(2 \times 1)$O/Cu(110) surface arising from an intramolecular electronic transition. The RA signal allows us to determine that the aromatic ring is aligned preferentially in the [110] direction. The intensity of the band is consistent with simple calculations and demonstrates that RAS is capable of determining the orientation and monitoring the deposition and removal of surface species at submonolayer detection levels. We expect that the capability of RAS to operate under higher pressure [19] and liquid phase conditions [20] can now be extended to investigate the structure and time dependent response of molecules, tagged

*Present address: Department of Chemistry and Laboratory for Surface Science and Technology, University of Maine, Orono, ME 04469.

†Present address: School of Chemistry, University of St. Andrews, St. Andrews KY16 9ST, Scotland, United Kingdom.

[1] D. E. Aspnes, Surf. Sci. **307–309**, 1017 (1994).

[2] Y. Borensztein, W. L. Mochan, J. Tarriba, R. G. Barrera, and A. Tadjeddine, Phys. Rev. Lett. **71**, 2334 (1993).

[3] W. L. Mochan, R. G. Barrera, Y. Borensztein, and A. Tadjeddine, Physica (Amsterdam) **207A**, 334 (1994).

[4] S. M. Scholz, F. Mertens, K. Jacobi, R. Imbihl, and W. Richter, Surf. Sci. **340**, L945 (1995).

[5] M. E. Pemble, N. Shukla, A. R. Turner, T. Bitzer, B. G. Frederick, K. J. Kitching, N. V. Richardson, J. Chem. Soc. Faraday Trans. **91**, 3627 (1995).

[6] P. Hofmann, K. C. Rose, V. Fernandez, A. M. Bradshaw, and W. Richter, Phys. Rev. Lett. **75**, 2039 (1995).

[7] B. G. Frederick, R. J. Cole, J. R. Power, C. C. Perry, Q. Chen, N. V. Richardson, P. Weightman, C. Verdozzi, D. R. Jennison, P. A. Schultz, and M. P. Sears, Phys. Rev. B (to be published).

[8] X. F. Jin, M. Y. Mao, S. Ko, and Y. R. Shen, Phys. Rev. B **54**, 7701 (1996).

[9] B. G. Frederick, C. Qiao, S. M. Barlow, N. G. Condon, F. M. Leibsle, and N. V. Richardson, Surf. Sci. **352–354**, 238 (1996).

[10] D. E. Aspnes, J. P. Harbison, A. A. Studna, and L. T. Florez, J. Vac. Sci. Technol. A **6**, 3291 (1988).

[11] R. J. Cole, B. G. Frederick, and P. Weightman, J. Vac. Sci. Technol. A (to be published).

[12] J. D. E. McIntyre and D. E. Aspnes, Surf. Sci. **24**, 417 (1971).

[13] V. Fernandez, D. Pahlke, N. Esser, K. Stahrenberg, O. Hunderi, A. M. Bradshaw, and W. Richter, Surf. Sci. **377**, 388 (1997).

[14] C. C. Perry, S. Haq, B. G. Frederick, and N. V. Richardson, Surf. Sci. Lett. (to be published).

[15] W. W. Simons, *The Sadtler Handbook of Ultraviolet Spectra* (Sadtler Research Laboratories, Philadelphia, PA, 1979).

[16] E. E. Koch and A. Otto, Chem. Phys. **3**, 370 (1974).

[17] *Handbook of Optical Constants of Solids,* edited by E. D. Palik (Academic Press, New York, 1985), Vol. 1.

[18] R. W. G. Wyckoff, *Crystal Structures* (Wiley Interscience, New York, 1960), Vol. 6, p. 454.

[19] I. Kamiya, D. E. Aspnes, H. Tanaka, L. T. Florez, J. P. Harbison, and R. Bhat, Phys. Rev. Lett. **68**, 627 (1992).

[20] V. L. Berkovits, A. O. Gusev, V. M. Lantratov, A. B. Pushnyi, V. P. Ulin, and D. Paget, Phys. Rev. B **54**, R8369 (1996).